

419. The Effect of p-Halogen Substituents on the Rate of Hydrolysis of Diphenylmethyl Chloride.

By G. KOHNSTAM.

The electromeric effect of halogen atoms is an important factor in the S_N1 hydrolysis of *para*-substituted diphenylmethyl chlorides, but only for fluorine is this effect large enough to make the substituent an overall donor of electrons relative to hydrogen. The rates follow the sequence $F > H > Cl > I > Br$ which arises entirely from changes in the activation energy; the entropy and heat capacity of activation are constant throughout the series. The substituent effects are usually independent of the nature of the solvent.

The use of linear free-energy relations in predicting the effect of *p*-halogen substituents on the rates of electron-demanding reactions is discussed.

It is generally agreed that halogen substituents attract electrons relative to hydrogen in the order $F > Cl > Br > I$ by the inductive effect,¹ as indicated by the acid strength of halogenoacetic acids² and the base strength of 2-halogenopyridines.³ In suitable systems these substituents can also release electrons in the same order by the mesomeric effect, as in the *p*-halogeno-phenols and -anilinium ions.⁴ Passage into the transition state of an electron-demanding reaction can invoke two polarisability effects in these substituents: the electromeric effect which is the time-variable analogue of the mesomeric effect and decreases in the same manner, and the inductomeric effect which depends on the ease of deformation of the outer electrons by an applied electric field and follows the sequence $I > Br > Cl > F$. At the beginning of the present work the order of the overall electron-release by halogen substituents in such reactions was not clear⁵ and further information was sought by investigating their effect on the rate of solvolysis of diphenylmethyl halides. There was good reason to believe that the reactions occur by the unimolecular mechanism, S_N1 ,⁶ and the transition state should therefore be particularly favourable to electromeric electron-release by *para*-substituents—the hydrolysis of the *p*-alkyl derivatives had already clearly demonstrated the order of the tautomeric hyperconjugative electron-release for these substituents.⁷ A preliminary summary of

¹ For a discussion of the polar effects of groups, see Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1952, chapter II.

² Watson, "Modern Theories of Organic Chemistry," Oxford Univ., 1937, p. 76.

³ Brown and McDaniel, *J. Amer. Chem. Soc.*, 1955, **77**, 3752.

⁴ Baddeley, Bennett, Glasstone, and Jones, *J.*, 1935, 1827.

⁵ de la Mare and Robertson, *J.*, 1948, 100.

⁶ Ref. 1, p. 325.

⁷ Hughes, Ingold, and Taher, *J.*, 1940, 949.

the present results has been reported⁸ and recent observations on similar systems^{9,10} are in substantial agreement with the present findings.

Most of the measurements were carried out on the hydrolysis of the diphenylmethyl chlorides, mainly in "70%" aqueous acetone. The parent bromide and its *p*-fluoro-derivative were also studied briefly in ethanol and "60%" ethanolic ether.* All the reactions were followed by the development of acidity, and the initial concentration of the substrate was never greater than 0.02M to avoid complications from mass-law and ionic-strength effects;¹¹ good first-order rate coefficients were always obtained. Triethylamine, sodium hydroxide, and sodium ethoxide (in the ethanolic solvents) at *ca.* 0.02M had only a small effect on the rate and did not upset the first-order kinetics, in agreement with earlier observations.¹² This demonstrates the unimolecular character of the reactions since the introduction of a better nucleophilic reagent than water or ethanol should yield a large increase in rate and second-order kinetics for bimolecular solvolysis.¹³ Steric considerations¹⁴ also render this alternative mechanism unlikely in the present systems.

RESULTS AND DISCUSSION

The Effect of Temperature on the Activation Parameters.—In "70%" aqueous acetone, energies and entropies of activation calculated from rate data at 0° and 25° were found to be greater than those calculated from data at 25° and 40° (see Table 4). Although a negative temperature coefficient is to be expected for these parameters in the solvolysis of organic halides,^{15,16} it is necessary to exclude the possibility that this observation arose from some systematic error such as evaporation of acetone from the solvent during the sampling of the runs at the highest temperature. The hydrolysis of the parent compound was therefore examined at two further temperatures. Energies and entropies of activation were calculated from data at adjacent temperatures, as previously described,^{15a} and are compared in Table 1 with the values obtained from the "best" straight lines, *E* against T_m and ΔS^\ddagger against $(\log T)_m$ where the subscript *m* refers to the mean of the experimental values of *T* or $\log T$. It can be seen that the figures are consistent with a constant value

TABLE 1. *Energies and entropies of activation for the reaction of diphenylmethyl chloride with "70%" aqueous acetone.*

Rates at 0.00°, 25.00°, and 40.12° are given in Table 4; at 14.99° and -10.90°, $10^6k = 146.1 \pm 0.241$ and 3.775 ± 0.0114 sec.⁻¹, respectively.

Temp. interval	40.12 — 25.00°	25.00 — 14.99°	14.99 — 0.00°	0.00 — -10.90°
$E_{\text{obs.}}$ (kcal. mole ⁻¹)	$20.13_3 \pm 0.04_9$	$20.64_8 \pm 0.05_1$	$20.94_3 \pm 0.04_5$	$21.53_3 \pm 0.06_8$
$E_{\text{calc.}}$ (kcal. mole ⁻¹)	20.142	20.589	21.034	21.495
$-\Delta S^\ddagger_{\text{obs.}}$ (cal. deg. ⁻¹)	8.20	6.40	5.26	3.03
$-\Delta S^\ddagger_{\text{calc.}}$ (cal. deg. ⁻¹)	8.18	6.60	4.95	3.16

$$dE/dT = -35.6 \pm 2.0 \text{ cal. mole}^{-1} \text{ deg.}^{-1}.$$

for the heat capacity of activation ($\Delta C^\ddagger = dE/dT - R$) over the whole temperature range, and that the value of ΔC^\ddagger is of the same magnitude as for other solvolytic reactions in mixed solvents.¹⁵ The apparent temperature-dependence of *E* and ΔS^\ddagger for the

* Throughout this paper an "x%" solvent refers to the mixture made up in the proportion *x* ml. of the solvent named last and 100 - *x* ml. of the other component.

⁸ Ref. 1, p. 332.

⁹ Brown and Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1906.

¹⁰ Fang, Hammond, and Kochi, *J. Amer. Chem. Soc.*, 1958, **80**, 563.

¹¹ Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979.

¹² Ward, *J.*, 1927, 2285.

¹³ Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603.

¹⁴ Hughes and de la Mare, *J.*, 1956, 845.

¹⁵ Bunsley and Kohnstam, (*a*) *J.*, 1956, 287, (*b*) *J.*, 1957, 4747.

¹⁶ Robertson, *Canad. J. Chem.*, 1955, **33**, 1536; *J. Chem. Phys.*, 1956, **25**, 375; Robertson, Hep-
polette, and Scott, *Canad. J. Chem.*, 1959, **37**, 803; Tommila, Tilikainen, and Voipio, *Ann. Acad. Sci. Fennicae*, 1955, *A*, II, 65.

hydrolysis of the *p*-halogen derivatives (see Table 4) can therefore be accepted as genuine, and the heat capacities of activation are given in Table 2 together with the values of the ratio $\Delta C^\ddagger/\Delta S^\ddagger$. It has been suggested that this ratio should be independent of the nature

TABLE 2. *Heat capacities of activation and $\Delta C^\ddagger/\Delta S^\ddagger$ for the reaction of $p\text{-X}\cdot\text{C}_6\text{H}_4\cdot\text{CHPhCl}$ with "70%" aqueous acetone.*

	X	H	F	Cl	Br	I
ΔC^\ddagger (cal. deg. ⁻¹) * ...	36.9 ± 2.9	64.5 ± 3.2	32.9 ± 2.8	40.6 ± 3.4	37.9 ± 1.9	
$\Delta C^\ddagger/\Delta S^\ddagger$ { 12.50° ...	6.3 ± 0.5	10.2 ± 0.5	5.5 ± 0.5	6.7 ± 0.6	6.3 ± 0.3	
{ 32.56° ...	4.5 ± 0.4	6.2 ± 0.3	4.0 ± 0.4	4.6 ± 0.4	4.4 ± 0.2	

* From the data in Table 3 on the assumption that *E* refers to the mean of the temperature interval for which it was calculated.

of the substrate in the S_N1 reactions of organic chlorides since the entropy and heat capacity of activation both reflect the increase in solvation on passage into the transition state,^{15b} and it can be seen that the present results are in agreement with this prediction, except for the *p*-fluoro-derivative. The behaviour of this compound probably arises from some systematic error in the measurements at 40.12° where the hydrolysis has a half-life of less than three minutes; this would affect the values of ΔC^\ddagger , ΔS^\ddagger (25—40.12°) and *E* (25—40.12°). It is noteworthy that ΔS^\ddagger (25—40.12°) is also anomalous for the *p*-fluoro-compound while ΔS^\ddagger (0—25°) has the value to be expected from the behaviour of the other halogen-derivatives (see p. 2069).

Substituent Effects and Solvent Changes.—The effect of *p*-halogen substituents on the rate of reaction of diphenylmethyl chloride with various solvents is shown in Table 3. In the present work the change in rate is independent of the nature of the solvent, and the results agree well with those of Berliner and Malter.¹⁷ However, reaction of the *p*-chloro-derivative with alcoholic solvents^{18,19} yields a value for k_{Cl}/k_H which differs from that

TABLE 3. *The effect of p-halogen substituents on the rate of reaction of diphenylmethyl chloride with various solvents at 25°.*

Solvent	k_F/k_H	k_{Cl}/k_H	k_{Br}/k_H	Solvent	k_F/k_H	k_{Cl}/k_H
60% Aq. dioxan ...	—	0.313	—	Methanol	—	0.47 ‡
60% Aq. acetone ...	—	0.337	—	Ethanol	1.79 *	0.42 ¶
70% Aq. acetone ...	1.86	0.328	0.251	Propan-2-ol	—	0.51 ‡
80% Aq. acetone ...	—	0.318 †	0.273 †	60% Ethanolic ether	1.93 *	—

* These experiments were carried out on the diphenylmethyl bromides. † Berliner and Malter.¹⁷

‡ Altscher, Baltzly, and Blackmann.¹⁸ ¶ Norris and Banta.¹⁹

now obtained in aqueous media, but the earlier results are also contradicted by the observation that *p*-halogen substitution in $\alpha\alpha$ -dimethylbenzyl chloride has the same effect on the rate of reaction with a number of aqueous and alcoholic solvents,^{9,20} and by results for the hydrolysis of α -methylbenzyl chlorides.²¹ Solvent-dependent substituent effects have been reported for the hydrolysis of benzyl toluene-*p*-sulphonates,^{10,22} but these reactions also show other anomalies (see below) and it may well be that the precise mechanism here depends on the solvent and substituent under consideration. It therefore seems reasonable to assume that changes in the rates of S_N1 reaction caused by *p*-halogen substituents are independent of the nature of the solvent. This conclusion is predicted by the equation of Winstein, Grunwald, and Jones²³ for the effect of solvent changes

¹⁷ Berliner and Malter; see Malter, Thesis, Bryn Mawr, 1952.

¹⁸ Altscher, Baltzly, and Blackmann, *J. Amer. Chem. Soc.*, 1952, **74**, 3649.

¹⁹ Norris and Banta, *J. Amer. Chem. Soc.*, 1928, **50**, 1804.

²⁰ Brown and Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1909; Brown, Okamoto, and Inukai, *ibid.*, 1958, **80**, 4972.

²¹ Mechelynck-David and Fierens, *Tetrahedron*, 1959, **6**, 232.

²² Fang, Hammond, Kochi, and Reeder, *J. Amer. Chem. Soc.*, 1958, **80**, 568.

²³ Winstein, Grunwald, and Jones, *J. Amer. Chem. Soc.*, 1951, **73**, 2700; Winstein, Grunwald, and Fainberg, *ibid.*, 1957, **79**, 4146.

on the rate of such reactions, and Streitwieser has pointed out that this equation appears to hold for structurally similar reactants.²⁴

The Effect of p-Halogen Substituents on the Activation Parameters.—The main results are summarised in Table 4. It can be seen that the rate decreases in the order F > H > Cl > I > Br and that this decrease is caused almost entirely by changes in the activation energy; the entropy of activation is constant within the limits of experimental error, and only ΔS^\ddagger (25—40·12°) for the *p*-fluoro-compound is anomalous (see p. 2068). While the rate sequence is in good agreement with the other findings for electron-demanding reactions (see Table 5), previous results suggest that both activation parameters are altered by *p*-halogen substitution.^{9,17,22,25,26} It must, however, be stressed that the changes in rate are not large and relatively small inaccuracies in the rate coefficients could therefore have been responsible for these observations; for example, the standard errors quoted by Berliner and Malter¹⁷ show that the entropy of activation in their experiments may well be independent of the nature of the substituent. A constant activation entropy is to be expected in S_N1 reactions if the transition state has the same degree of charge development and the same degree of solvation for all the compounds under consideration, and it is noteworthy that more polar substituents in diphenylmethyl chloride^{7,27} and in $\alpha\alpha$ -dimethylbenzyl chloride²⁸ also affect the rate mainly through the activation energy. In benzyl toluene-*p*-sulphonates, however, the effect of substituents on the rate of hydrolysis is mainly reflected in the entropy of activation.²² Similar observations for the hydrolysis of benzyl chlorides have already led to the conclusion that the parent compound and its *p*-methyl derivative do not react by precisely the same mechanism^{15b,29} and it may well be that analogous considerations apply to the toluenesulphonates. Admittedly, these compounds are usually assumed to undergo S_N1 solvolysis, but Hammond and his co-workers found that several of their results are not wholly consistent with this view.²²

Polar Effects.—In the hydrolysis of diphenylmethyl chlorides, electron-releasing substituents will tend to stabilise the transition state relatively to the initial state, and electron-attracting substituents will have the converse effect. It can therefore be concluded

TABLE 4. Kinetic data for the reaction of *p*-X·C₆H₄·CHPhCl with "70%" aqueous acetone.

(Errors quoted are standard deviations from the final mean. k in sec.⁻¹, E in kcal. mole⁻¹, ΔS in cal. deg.⁻¹).

X =	H	F	Cl	Br	I
10 ⁶ k { 40-12° 2527 ± 7·76 25-00° 493·1 ± 1·14 * 0-00° 19·63 ± 0·0789	(4291 ± 20·5)	873·0 ± 3·02	667·9 ± 1·82	754·8 ± 1·82	139·2 ± 0·197
k_X/k_H at 25°	1·00	1·86	0·328	0·251	0·284
E { 0-25° 20·83 ₃ ± 0·03 ₁ 25-40° 20·13 ₃ ± 0·04 ₉	20·29 ₁ ± 0·01 ₆	21·40 ₆ ± 0·02 ₁	21·54 ₇ ± 0·02 ₈	21·47 ₆ ± 0·01 ₇	20·75 ₆ ± 0·03 ₄
$-\Delta S^\ddagger$ { 0-25° ... 5·90 ± 0·10 25-40° 3·20 ± 0·16	6·31 ± 0·05	6·01 ± 0·07	6·07 ± 0·09	6·06 ± 0·06	8·61 ± 0·11

* At 25·05°. † At 25·10°. ¶ The figures in parentheses involve a rate coefficient which may be subject to error (see p. 2068).

that the overall electron-release by the substituents follows the same sequence as the rate, *viz.*, F > H > Cl > I > Br. Except for the inversion of I and Br, this is also the order of tautomeric electron-release and it therefore appears that this effect is invoked to a considerable extent in the present reactions. This view is supported by studies of the hydrolysis of $\alpha\alpha$ -dimethylbenzyl chlorides;⁹ here the relative rates (k_X/k_H) for

²⁴ Streitwieser, *Chem. Rev.*, 1956, **56**, 618.

²⁵ Bennett and Jones, *J.*, 1935, 1815.

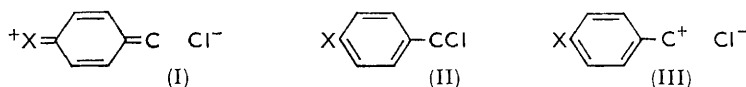
²⁶ Branch and Nixon, *J. Amer. Chem. Soc.*, 1936, **58**, 492.

²⁷ Hughes, Ingold, and Kohnstam, unpublished work.

²⁸ Brown, Brady, Grayson, and Bonner, *J. Amer. Chem. Soc.*, 1957, **79**, 1897.

²⁹ Tommila, Paakkala, Virtanen, Erva, and Varila, *Ann. Acad. Sci. Fennicae*, 1959, *A*, II, 91.

p-halogen derivatives are similar to those now observed, but the *meta*-derivatives, where tautomeric effects cannot be fully operative, show very much smaller relative rates. It seems highly probable that the present tautomeric electron-release is largely electromeric in origin, *i.e.*, that it mainly arises in the transition state of hydrolysis. Here the electron-demand at the reaction centre is much greater than in the initial state, so that any substituent with a capacity for tautomeric electron-release can be expected to be a better electron-donor under these conditions. In valence-bond language, this type of electron



release can be represented by a contribution of structure (I) to the actual structure of the system. In the initial state, the main canonical form (II) has a much lower energy than structure (I) which can therefore be expected to contribute little to the final resonance hybrid. Structure (I) may, however, participate significantly in the structure of the transition state since a capacity for tautomeric electron-release by the group X can result in an energy for this structure which does not differ greatly from that of structure (III).

The conclusion that *p*-halogen groups show considerable electromeric electron-release in the present reactions is not inconsistent with the fact that the *p*-iodo-compound is hydrolysed faster than the *p*-bromo-derivative (see Table 4). The overall polar effects of the halogens, which control the rate, are the resultants of two opposing factors, both of which decrease in the order $F > Cl > Br > I$, namely, tautomeric electron-release and inductive attraction. A regular sequence for the rates is thus not necessarily required by the present interpretation. A small contribution from the inductomeric effect (which decreases in the order $I > Br > Cl > F$) cannot be excluded for the *p*-iodo-compound, but the results show clearly that electromeric electron-release is the principal polarisability effect operating in the present reactions.

It is noteworthy that only the *p*-fluoro-group can act as an overall donor of electrons, relative to hydrogen (see Table 4). Chlorine can act as an overall electron-releasing group in S_N1 reactions when it is placed at the reaction centre^{15a, 30, 31} and, to a smaller extent, when it is a γ -substituent in allyl chloride,³¹ but it invariably acts as an overall electron-attractor in the *para*-position of aryl and arylalkyl chlorides (see Table 5). It must therefore be concluded that tautomeric effects (or, alternatively, demands for electrons at reaction centres) are not relayed efficiently through conjugated systems.

Comparison with Other Systems.—The effect of *p*-halogen substituents on the rates and equilibria of processes facilitated by electron-release towards the reaction centre, and structurally favourable to the operation of tautomeric effects, are compared in Table 5. It can be seen that the present results are in good qualitative agreement with previous observations (which have often been quoted to establish the variation of the tautomeric effect in the halogens), but there are a number of quantitative differences which it is now necessary to discuss.

The figures in Table 5 show that k_F/k_H varies by a factor of 8 in the reactions under consideration. Fluorine attracts electrons by the inductive effect, but this attraction is much less sensitive to changes in the electron-demand at the site of substitution than electron-donation by the tautomeric effect, and it is therefore to be expected that a *p*-fluoro-group will become a progressively more efficient overall donor of electrons as this demand increases. The data for the S_N1 hydrolysis of arylalkyl chlorides (reactions 6—9) support this conclusion. As a first approximation it can be assumed that the degree of charge

³⁰ Olivier and Weber, *Rec. Trav. chim.*, 1934, **53**, 869; Evans and Hamann, *Trans. Faraday Soc.*, 1951, **47**, 52; Hine and Lee, *J. Amer. Chem. Soc.*, 1951, **73**, 22; Andrews and Kaeding, *ibid.*, p. 1007; Bensley and Kohnstam, *J.*, 1955, 3408.

³¹ Vernon, *J.*, 1954, 423.

development in the transition state, and hence the electron-demand at the reaction centre, is the same for all these reactions, but that the electron-demand at the site of substitution will decrease with increasing facility for electron-release by other groups attached to the central carbon atom. α -Methyl groups are less efficient in this respect than α -phenyl groups, and k_F/k_H should therefore decrease on passing from reaction 6 to reaction 9,

TABLE 5. *The effect of p-halogen substituents on the rates (or equilibrium constants) of electron-demanding reactions.*

	X =	K_X/K_H or k_X/k_H			
		F	Cl	Br	I
1. $X \cdot C_6H_4 \cdot O^- + H^+ \rightleftharpoons X \cdot C_6H_4 \cdot OH$, "30%" aq. ethanol, 25° ⁴ ...	F	1.23	0.242	0.206	0.146
2. $X \cdot C_6H_4 \cdot NH_2 + H^+ \rightleftharpoons X \cdot C_6H_4 \cdot NH_3^+$, "30%" aq. ethanol, 25° ⁴	F	0.952	0.229	0.174	0.120
3. $X \cdot C_6H_4 \cdot CH(OH) \cdot CN \rightleftharpoons X \cdot C_6H_4 \cdot CHO + HCN$, ethanol, 25° ^a ...	F	1.42	0.865	0.732	0.703
4. $X \cdot C_6H_4 \cdot CH_2Cl \longrightarrow X \cdot C_6H_4 \cdot CH_2 \cdot OH$, "50%" aq. acetone, 69.8° ²⁵	F	1.7	0.59	0.46	0.44
5. $X \cdot C_6H_4 \cdot CH_2 \cdot O \cdot S_2 \cdot C_6H_4 \cdot Me \longrightarrow X \cdot C_6H_4 \cdot CH_2 \cdot OH$, "55.6%" aq. acetone, 25° ¹⁰	F	2.58	0.537	0.433	0.494
6. $X \cdot C_6H_4 \cdot CHMeCl \longrightarrow X \cdot C_6H_4 \cdot CHMe \cdot OH$, "50.7%" aq. dioxan, 25° ²¹	F	3.63*	0.316*	—	—
7. $X \cdot C_6H_4 \cdot CMe_2Cl \longrightarrow X \cdot C_6H_4 \cdot CMe_2 \cdot OH$, "90%" aq. acetone, 25° ⁹	F	2.14	0.305	0.208	0.244
8. $X \cdot C_6H_4 \cdot CHPhCl \longrightarrow X \cdot C_6H_4 \cdot CHPh \cdot OH$, "70%" aq. acetone, 25° ^b	F	1.86	0.328	0.251	0.284
9. $X \cdot C_6H_4 \cdot CPh_2Cl \longrightarrow X \cdot C_6H_4 \cdot CPh_2 \cdot OH$, "60%" ethanolic ether, 25° ²⁸	F	0.76	0.32	0.28	0.34
10. $X \cdot C_6H_4 \cdot CH(OH) \cdot CH \cdot CHMe \longrightarrow X \cdot C_6H_4 \cdot CH \cdot CH \cdot CHMe \cdot OH$, "60%" aq. dioxan, 30° ^c	F	0.843	0.239	0.198	—
11. $X \cdot C_6H_5 \longrightarrow p \cdot X \cdot C_6H_4 \cdot NO_2$, acetyl nitrate, 25° ^d	F	0.79	0.14	0.11	0.60
12. $X \cdot C_6H_5 \longrightarrow p \cdot X \cdot C_6H_4 \cdot Cl$, acetic acid, 25° ^e	F	6.5	0.36†	0.25†	0.50†
13. $1 \cdot X \cdot C_{10}H_8 \longrightarrow 1,4 \cdot X \cdot C_{10}H_7 \cdot Br$, acetic acid, 25° ⁵	F	3.7	0.13	0.09	0.22
14. $X \cdot C_6H_4 \cdot B(OH)_2 \longrightarrow X \cdot C_6H_4 \cdot Br$, "20%" acetic acid, 25° ^f	F	2.81	0.539	0.413	0.498

* These figures were obtained by extrapolation from data at higher temperatures. † These figures may be subject to some inaccuracy as they depend on an estimate for the percentage of *p*-chlorination.

^a Baker and Hopkins, *J.*, 1949, 1089. ^b Present work. ^c Braude and Stern, *J.*, 1947, 1096. ^d Ref. 1, pp. 246, 260. ^e de la Mare, *J.*, 1954, 4450; de la Mare, Robertson, and Swedlund, *J.*, 1952, 782. ^f Kuivila and Hendrichson, *J. Amer. Chem. Soc.*, 1952, **74**, 5068; Kuivila and Benjamin, *ibid.*, 1955, **77**, 4834.

as observed; in the hydrolysis of triphenylmethyl chloride the electron-demand on the substituent is so small that fluorine acts as an overall attractor of electrons. On this view, the S_N1 hydrolysis of benzyl chloride and benzyl toluene-*p*-sulphonate should be associated with even larger values of k_F/k_H than reaction 6, and the results for reactions 4 and 5 can be explained by noting that reaction 4 is largely, if not entirely, bimolecular,^{15b} and that reaction 5 is probably not wholly unimolecular (see p. 2069). If the effect of more polar groups, such as *p*-methyl and *p*-nitro, on the rate of reaction is taken as a measure of the electron-demand at the site of substitution, k_F/k_H generally decreases with an increase in this demand, as expected.

The principal exceptions to this rule are the *para*-nitration of halogenobenzenes (reaction 11) and the benzaldehyde-cyanohydrin equilibrium (reaction 3). In reaction 11, k_F/k_H is lower than would have been expected from k_{Me}/k_H , and k_I/k_H is abnormally high; it has been pointed out by several workers that electromeric electron-release is apparently not favoured in the transition state of this reaction but that the system is favourable to the operation of the inductomeric effect.³² In reaction 3, fluorine appears to act as an overall donor of electrons, but the polar requirements of the equilibrium are not unambiguous; ³³ K_{Me}/K_H is only 50% greater than K_F/K_H and $K_{NO_2} \approx K_I$. An examination of the rates of the forward and back reactions shows that both are facilitated by electron-attracting substituents. A *p*-fluoro-group enhances both rates and does not, therefore, act as an overall electron-donor in either of the reactions.

³² Berliner and Berliner, *J. Amer. Chem. Soc.*, 1954, **76**, 6279, and references cited in this paper.

³³ Baker and Hopkins, *J.*, 1949, 1089.

The other halogens have much the same effect on the rates of most of the reactions listed in Table 5. Deviations from this normal behaviour are shown by reactions 1—5, 11, 13, and 14, but these probably arise from special causes. It has already been pointed out in the previous paragraph that equilibrium constants do not necessarily reflect the polar properties of substituents (reactions 1—3) and the unusually high values of k_X/k_H for the three higher halogens in reactions 4, 5, and 14 may arise from a weaker demand for electrons at the reaction centre than in the parent compound; these reactions are always less sensitive to electron-attracting substituents than would have been expected from the effect of electron-donating groups on their rates. The low value of k_X/k_H for chlorine and bromine in reaction 11 probably results from the absence of an appreciable electromeric effect (see preceding paragraph) but it is difficult to see how this explanation can be applied to the similar observation in reaction 13 where k_F/k_H is relatively large.

Chlorine, bromine, and iodine act as overall electron-attractors in all the reactions listed in Table 5. Since these substituents release electrons by the tautomeric effect to a much smaller extent than fluorine does, the observation that they have almost the same effects on the rates of different reactions suggests that any changes in the magnitude of the tautomeric electron-release, resulting from changes in the demand for electrons, are only sufficient to cancel the altered sensitivity of the reaction to the presence of electron-attracting groups. Iodine usually retards electrophilic reactions less than nucleophilic reactions, probably because the former processes invoke stronger inductomeric effects.

The Hammett Equation.—The effect of *meta*- and *para*-substituents on the rates of chemical reactions has often been discussed in terms of the Hammett equation, $\log(k_X/k_H) = \sigma\rho$,³⁴ where the constant σ represents the effect of the substituent on the electron density at the reaction centre and depends only on the nature of that substituent, and the constant ρ is a measure of the sensitivity of the rate (or equilibrium) to changes in the electron density and depends only on the reaction under consideration. The standard σ -values,³⁵ however, reflect to a greater extent the inductive than the tautomeric effect of substituents,³⁶ and several workers have reported that reactions favourable to the operation of tautomeric effects require either a modified Hammett equation, or substituent constants (σ) which differ from the standard values.^{35,37} Brown and his co-workers have recently proposed a set of such substituent constants (σ^+) for reactions facilitated by electron-release towards the reaction centre and found that these constants could be applied with a fair degree of success to a variety of such reactions.^{37b} The validity of the σ^+ -values for predicting the effect of *p*-halogen substituents is considered below.

Brown's σ^+ -values are based on the results observed in the hydrolysis of $\alpha\alpha$ -dimethylbenzyl chlorides (Table 5, reaction 7), and indicate that a *p*-fluoro-group should act as an overall donor of electrons while the other halogens behave as overall electron-attractors in the *para*-position. Thus, a reaction which is accelerated more than reaction 7 by a *p*-fluoro-substituent should also be retarded more than this reaction by *p*-chloro-, *p*-bromo-, and *p*-iodo-groups, and *vice versa*. The results in Table 5, however, show that these requirements are only rarely obeyed and it is also noteworthy that fluorine acts as an overall electron-attracting group in four of the reactions listed, contrary to the predictions

³⁴ Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 188.

³⁵ Jaffé, *Chem. Rev.*, 1953, **53**, 191.

³⁶ de la Mare, *J.*, 1954, 4450; de la Mare, Robertson, and Swedlund, *J.*, 1952, 782.

³⁷ (a) Baxter, Martin, and Pearson, *J. Org. Chem.*, 1952, **17**, 1511; Taft, "Steric Effects in Organic Chemistry," J. Wiley and Sons, New York, 1956, chapter 13; Deno and Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3051; Roberts and Moreland, *ibid.*, 1953, **75**, 2167; Miller, *J. Austral. Chem.*, 1956, **9**, 61; (b) Brown and Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1913; 1958, **80**, 4979; *J. Org. Chem.*, 1957, **22**, 485.

of the σ^+ -values. Reactions 3, 4, 8, and 13 proceed in the expected manner but it is noteworthy that substituent effects in reaction 8 are always extremely similar to those in reaction 7. Reaction 13 should probably not have been included in this discussion as it involves substitution in naphthalene and not in benzene; the equilibrium constants of reaction 3 do not reflect the polar effects of substituents (see p. 2071) and should therefore not be predicted by σ^+ ; and the precise mechanism of reaction 4 probably depends on the nature of the substituent (see p. 2069).

A more quantitative test is obtained by calculating the reaction constant, ρ , from the effect of *p*-chloro- and *p*-bromo-substituents and the published values of σ^+ (the two ρ -values so obtained are always in good agreement with each other), and hence calculating k_F/k_H and k_I/k_H . Reasonable agreement between the observed and the calculated values of k_F/k_H is again obtained for reactions 3, 4, 8, and 13 but as was pointed out in the preceding paragraph this does not necessarily support the validity of the σ^+ treatment. In the other reactions, k_F/k_H differs by a factor of 1.7—4 from the calculated value; k_I/k_H is twice as large as the calculated values for reactions 12 and 13, and five times as large for reaction 11. These differences are of the same magnitude as the changes in rate caused by the substituents, and it is therefore felt that the effects of *p*-halogen substituents are more profitably discussed by using Ingold's approach³⁸ of considering the polarisation and polarisability effects, and the reaction mechanism. This conclusion is in general agreement with that already reached by Eaborn³⁹ who pointed out that the effect of *p*-halogen substituents on the rates of electrophilic reactions cannot be accommodated by an equation of the Hammett type.

EXPERIMENTAL

Preparation of Materials.—The 4-halogenobenzophenones were obtained by Friedel-Crafts reactions from benzoyl chloride and the halogenobenzenes,⁴⁰ except for the 4-iodo-derivative

TABLE 6.

Compound	M. p.			Compound	M. p.		
	obs.	lit.	ref.		obs.	lit.	ref.
F·C ₆ H ₄ ·COPh	48.2°	48.5° *	a	C ₆ H ₅ ·CHPh·OH	67.8°	67.8°, 69°	d
Cl·C ₆ H ₄ ·COPh	76.2	75.7, 77.5	b	F·C ₆ H ₄ ·CHPh·OH	48.4	48.0	c
Br·C ₆ H ₄ ·COPh	81.2	82.5	41	Cl·C ₆ H ₄ ·CHPh·OH	62.3	62.0	e
I·C ₆ H ₄ ·COPh	100.5	102	c	Br·C ₆ H ₄ ·CHPh·OH	64.9	65.0, 66	e, g
				I·C ₆ H ₄ ·CHPh·OH	74.2	73	g

Compound	M. p. or b. p./mm.			Found (%)		Formula	Calc. (%)	
	obs.	lit.	ref.	C	H		C	H
C ₆ H ₅ ·CHPhCl	19.6°	20.5°	12	77.6	5.5	C ₁₃ H ₁₁ Cl	77.0	5.4
F·C ₆ H ₄ ·CHPhCl	128.5°/1.5	—	—	70.8	4.6	C ₁₃ H ₁₀ ClF	70.8	4.5
Cl·C ₆ H ₄ ·CHPhCl	129°/1.6	172°/6	19	66.3	4.3	C ₁₃ H ₁₀ Cl ₂	65.8	4.2
Br·C ₆ H ₄ ·CHPhCl	22.5	147°/2	19	55.7	3.7	C ₁₃ H ₁₀ ClBr	55.4	3.55
I·C ₆ H ₄ ·CHPhCl	47.5	—	—	47.0	3.2	C ₁₃ H ₁₀ ClI	47.5	3.0
C ₆ H ₅ ·CHPhBr	44.3	45	h	—	—	—	—	—
F·C ₆ H ₄ ·CHPhBr	20.2	—	—	59.5	3.6	C ₁₃ H ₁₀ BrF	58.9	3.8

* A considerably higher m. p. had been reported by Koopal (ref. c), but a repetition of his synthesis, starting with *p*-fluorotoluene prepared from toluene-*p*-diazonium borofluoride (Balz and Schiemann, *Ber.*, 1927, **60**, 1186), had the same m. p. and as our original sample and an undepressed mixed m. p. Refs.: (a) Dunlop and Gardener, *J. Amer. Chem. Soc.*, 1933, **55**, 1665. (b) Kollaritz and Mertz, *Ber.*, 1873, **6**, 547; Wegerhoff, *Annalen*, 1891, **262**, 6. (c) Koopal, *Rec. Trav. chim.*, 1915, **34**, 156. (d) Nef, *Annalen*, 1897, **298**, 9. (e) Mihailescu and Caragea, *Bull. Sect. Sci. Acad. roumaine*, 1929, **12**, 7; Montagne, *Rec. Trav. chim.*, 1920, **39**, (f) 492, (g) 350. (h) Courtot, *Ann. Chim. (France)*, 1916, **5**, 80; Norris, Thomas, and Brown, *Ber.*, 1910, **43**, 2959.

³⁸ Ref. 1, ch. 6, 7, 13.

³⁹ Eaborn, *J.*, 1956, 4858.

⁴⁰ Montagne, *Rec. Trav. chim.*, 1907, **26**, 263, 264, 266; 1908, **27**, 336.

which was prepared from 4-aminobenzophenone by the Sandmeyer reaction.⁴¹ The crude ketones were purified by distillation at reduced pressure, or by recrystallisation from ligroin (b. p. 100—120°), light petroleum (b. p. 40—60°), or ethanol, and were converted into the corresponding diphenylmethanols by reduction with aluminium isopropoxide.⁴² After recrystallisation from ligroin, the alcohols were converted into the diphenylmethyl chlorides by passing a stream of dry hydrogen chloride into their ethereal solutions, in the presence of anhydrous calcium chloride.⁷ After removal of the ether and excess of acid, the chlorides were purified by distillation at low pressure or by recrystallisation from light petroleum; the hydrolysable chloride was always 99.5—100% of the theoretical amount. Diphenylmethyl bromide and its *p*-fluoro-derivative were similarly prepared from the alcohols by passing dry hydrogen bromide into their solutions in light petroleum in the presence of anhydrous lithium bromide; the hydrolysable bromide was again within 99.5—100% of the theoretical amount, after recrystallisation of the product from the same solvent. Physical properties and analytical figures for all these compounds are given in Table 6.

Acetone and ethanol were purified as previously described.^{15a} Ether was dried over sodium wire and distilled from a fresh batch of sodium. Aqueous acetone and ethanol-ether were made up by volume,^{15a} and solutions of sodium hydroxide and ethoxide were prepared by adding a weighed amount of the clean, dry metal and the amount of water (or ethanol) necessary to replace the losses resulting from the reaction with the metal.

Rate Measurements.—The methods employed in the measurement of solvolytic rates were similar to those already described.¹⁵ Kinetic runs were carried out in duplicate or triplicate, and details of a typical run, the hydrolysis of *p*-fluorodiphenylmethyl chloride in "70%" aqueous acetone at 0°, are annexed (*t* in sec., *k* in sec.⁻¹).

5 ml. samples titrated with 0.00568N-NaOH							
10 ⁻³ <i>t</i>	0	1.200	2.400	3.600	5.400	7.200	9.000
Titre	0.48	1.29	2.06	2.80	3.82	4.72	5.68
10 ³ <i>k</i>	—	3.973	3.973	3.992	3.957	3.890	3.955
10 ⁻³ <i>t</i>	10.80	14.40	18.00	21.60	28.80	∞	
Titre	6.49	8.08	9.33	10.50	12.27	17.84	
10 ³ <i>k</i>	3.935	3.999	3.962	3.985	3.945	—	

10³*k* (mean) = 3.961 ± 0.0096; a duplicate run (10 readings) gave 10³*k* = 3.963 ± 0.0101.

A number of different batches of "70%" aqueous acetone were employed. Each batch was tested by noting its rate of reaction with diphenylmethyl chloride, and the rate coefficients in Table 4 have been corrected to refer to the same batch of solvent.

The products of the hydrolysis of *p*-fluoro- and *p*-iodo-diphenylmethyl chloride in "70%" aqueous acetone were proved to be the corresponding alcohols by methods analogous to those described by Hughes, Ingold, and Taher,⁷ yields being essentially quantitative, and the products had the same m. p.s as the authentic samples and undepressed mixed m. p.s. There was no evidence of reversibility in any of the reactions studied; the acidity of solutions 0.2M in the alcohol and hydrochloric acid was unchanged after periods corresponding to ten "half-lives" in the hydrolysis of the corresponding chlorides.

The author is deeply indebted to Sir Christopher Ingold, F.R.S., and Professor E. D. Hughes, F.R.S., for suggesting this problem, and for continued help and encouragement. The award of a Tuffnell Scholarship by the Committee of University College, London, and of a grant by the Ministry of Education under the Further Education and Training Scheme, is also gratefully acknowledged.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER STREET, LONDON, W.C.1.
[Present address: UNIVERSITY SCIENCE LABORATORIES,
SOUTH ROAD, DURHAM.]

[Received, November 25th, 1959.]

⁴¹ Gattermann, "Laboratory Methods of Organic Chemistry," Macmillan, London, 1941, p. 248.

⁴² Lund, *Ber.*, 1937, **70**, 1520.